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The oxidation of metallic arsenides
by the electric current.

by
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The oxidation of metallic arsenides
by the electric current.

The decomposition of minerals and their subsequent oxidation by means of the electric current is a product of very recent origin.

By reference to the literature of the subject, it will be found that the first attempt in this direction was made by Dr. Smith in a paper published in the "Berichte der Deutschen Chemischen Gesellschaft" vol ~~XXX~~ p. 1019, in which the author has successfully completed the decomposition of chalcopyrite and gives the results of some preliminary investigations on chromite.

In a later and more exhaustive paper in the same journal (vol. ~~XXX~~ p. 2276). Dr. Smith has published his

researches on the decomposition of other sulphides, and has proven conclusively, that oxidations by the electric current, give results as quantitatively correct, as those obtained by any wet or fusion method. In a still later paper by the same author (American Chemical Journal, vol. 13. No 6), Experiments on various kinds of chromite, indicate that the decomposition of this mineral is complete, if the conditions prescribed are closely followed. At present this completes the literature of the subject, and judging from the success, thus far obtained, it was deemed advisable, to attempt the oxidation of the native arsenides, with the hope that the results would be similarly fruitful. These

results and the methods used for obtaining them, will be found appended below.

The apparatus used for this purpose was the same as that described by Dr Smith in the *Berichte der Deutschen Chemischen Gesellschaft* vol. XXIII, p. 2276), and the method of using it, was also substantially the same. The current generated from four storage cells of the Tubau type, was passed through the resistance frame, then through a Kohlrausch amperemeter, and lastly up through the metal crucible, the latter being in all cases the positive pole at the beginning of the operation. As for the oxidations, the time required, the strength of current

(4)

etc. differed in each mineral respectively. For this reason, no general plan can be prescribed, but the details of the work will be found for each mineral, under its respective heading.

Gersdorffite. (Mn, Fe) As S.

The sample used for the decomposition came from Sphauming. The method of procedure was as follows:-

In a nickel crucible, $1\frac{1}{4}$ inches high, and $1\frac{3}{8}$ inches wide, 25-30 grams of solid caustic potash were placed. The contents of the crucible were then heated until fusion took place, when the Gersdorffite was carefully added. A current registering one ampere was passed through the mass for twenty minutes, the

(5)

crucible being the anode. Towards the end of the operation, the current was reversed for three minutes, to remove any particles of mineral that might have been enclosed in the metal deposited on the cathode. After breaking the current, the crucible was allowed to cool, the contents then thoroughly disintegrated with hot water, and the resultant insoluble material, (nickel and iron oxides) filtered off. The clear filtrate was acidulated with concentrated hydrochloric acid, and then made strongly alkaline with ammonium hydrate. The precipitate (silica and alumina from the caustic potash) which formed on the addition of the latter reagent, was filtered

off, and magnesia mixture added. The precipitate of magnesium ammonium arsenate which formed after standing twelve hours, was filtered off, dissolved in dilute hydrochloric acid, reprecipitated with ammonium hydrate, filtered, dried, ignited in a platinum crucible, and weighed in the manner prescribed for this determination. The results obtained were as follows:-

- (1). 0,2777 gram of gersdorffite gave 0,2853 gram of magnesium pyroarsenate = 49.73% arsenic.
- (2). 0,1137 gram of gersdorffite gave 0,1173 gram of magnesium pyroarsenate = 49.94% arsenic.
- (3). 0,2548 gram of gersdorffite was dissolved in nitric acid, evaporated to dryness, the residue taken up

in hydrochloric acid, and the arsenic acid reduced with sulphurous acid. After removing the excess of sulphurous acid by gentle warming, the solution was precipitated with hydrogen sulphide, the resulting arsenious sulphide filtered off, dissolved in nitric acid, the solution made alkaline, with ammonium hydrate magnesia mixture added, and the arsenic determined in the same manner as that given above.

0.2617 gram of magnesium pyroarsenate was found = 49.72% arsenic.

The insoluble residues remaining after the fusions were dissolved in water were dissolved in nitric acid, and evaporated to dryness, Hydrochloric acid was then added, and hydrogen sulphide passed

through the solution for several hours, without the formation of any precipitates of sulphide of arsenic, showing that the mineral had been completely decomposed.

Niccolite, Ni. As.

With this mineral an attempt was made to see what effect currents of greater intensity than the one used above, would have on the decomposition. It was hoped that with a current of greater strength, the decomposition could be effected in a shorter period of time, but as will be seen, the results, in so far as a diminution of the time limit is concerned, are practically of a negative order.

(9)

Two samples of the finely ground niccolite were subjected to a current which varied from $1\frac{1}{2}$ - $1\frac{3}{4}$ amperes, for twenty minutes, and without any reversal of the current, 25-30 grams of caustic potash were used. In both cases did the residues which remained after disintegrating the fused mass with water, show the presence of arsenic, on treating the residues with nitric acid, evaporating to dryness, and subsequently adding hydrochloric acid and hydrogen sulphide. The presence of arsenic in the residues is probably due to the fact that the greater strength of current used in the decomposition, deposits larger quantities of metallic

nickel on the Kathode, enclosing at the same time appreciable quantities of undecomposed mineral.

A much weaker current was now tried. Two samples of the mineral were subjected to a current of $\frac{1}{2}$ an ampere for twenty minutes, 25-30 grams of caustic potash being used. The results were the same as in the two previous cases, arsenic being found in both of the residues.

The time limit was now extended with more satisfactory results, the manner of decomposition being as follows:-

A current of one ampere was allowed to pass through the fused mass for twenty-five

(11)

minutes, the current passing up through the crucible. At the end of this time, the current was reversed for five minutes, to remove any metal or any undecomposed mineral that may have attached itself to the platinum wire. The subsequent operations of extracting the alkaline arsenate, and weighing it as magnesium-pyroarsenate, were similar to those already given under Gersdorffite, with the exception that instead of filtering the precipitate of magnesium ammonium arsenate through filter paper, and igniting it in a platinum crucible, the precipitate was filtered directly through a porcelain Gooch crucible, of the

pattern recommended by Professor Caldwell, owing to the fine granular condition of the precipitate, this requires some care, particularly if the filter pump be used to hasten the filtration. The best results were obtained by first placing a layer of glass wool in the crucible, and covering this with a layer of asbestos. After filtering, the crucible with its contents, was first dried on a hot iron plate, until all moisture was removed, and then gradually heated over a Bunsen burner for an hour. In this time all the precipitate will be converted into magnesium pyroarsenate. It is hardly necessary to state that the flame from the burner

should not be allowed to enter the crucible through the openings in the bottom, lest a partial reduction of the magnesium pyroarsenate ensue. It was also found advisable to allow the crucibles to stand for twelve hours after ignition, since the constant changes in temperature, made appreciable differences in the weighings. The results were as follows:-

(1) 0.1209 gram of niccolite ^{gave} 0.1301 gram of magnesium pyroarsenate = 52.09% arsenic.

(2) 0.1540 gram of niccolite gave 0.1672 gram of magnesium pyroarsenate = 52.55% arsenic.

The residues left after disintegrating the fusions with water, gave no reactions for arsenic.

They both had a peculiar crystalline appearance, resembling minute plates. They dissolved in nitric acid without any evolution of nitrous fumes, and are probably an oxide of nickel.

Another sample of the ore was dissolved in nitric acid, the excess of acid evaporated, ammonium hydroxide added along with magnesia solution, and the arsenic determined in the usual manner as magnesium pyroarsenate, the weighing being made in a platinum crucible with the following result:-

0.2611 gram of niccolite gave
 0.2833 gram of magnesium
 pyroarsenate = 52.52 % of
 metallic arsenic.

Arsenopyrite. Fe As S .

The conditions under which arsenopyrite is decomposed are very similar to those of niccolite. The quantity of caustic potash used, the time of decomposition, the reversal of the current etc. are precisely the same, the only difference in the conditions, lying in the fact, that in the decomposition of arsenopyrite, it was found that the current might vary from one to one and a half amperes, without affecting the decomposition. The method of determining the arsenic, as far as the Gooch Crucible etc. is concerned, was the same as under niccolite.

The results found were as follows:—

(1)

0,2168 gram of arsenopyrite gave
0,1729 gram of magnesium pyro-
arsenate = 38.6% arsenic.

2)

0,1709 gram of arsenopyrite gave
0,1356 gram of magnesium pyro-
arsenate = 38.41% arsenic.

The residues from the fusions
treated similarly to those under
hecolite showed no traces of
arsenic.

0,2306 gram of the ore was dissolved
in concentrated nitric acid, evap-
orated to dryness, treated with
hydrochloric acid and water,
and any insoluble matter re-
maining filtered off. The solution
was then reduced with sulphur-
ous acid, the excess of the
latter removed by boiling, and
the arsenic precipitated by

hydrogen sulphide. The solution was then allowed to stand until the odor of hydrogen sulphide was barely perceptible, and then filtered on a porcelain Gooch crucible, washed with cold water, carbon disulphide and alcohol dried at 100°C . and weighed. The result was 47.73% Arsenic. As the high result could be due to but one cause, viz. the presence of sulphur in the precipitate, repeated treatments with carbon disulphide and alcohol were given the latter, but without avail. The precipitate was eventually dissolved in nitric acid, and the arsenic thrown out with magnesia solution. Found:- 0.1856 gram of magnesium pyroarsenate =

38.96% metallic arsenia.

It will be seen from this, that the determination of arsenia directly as arsenious sulphide, by weighing in a porcelain Gooch crucible is not practicable. The method was tried with various other minerals, and in but one case, were the results within limits, due more to accident, than to any virtues of the method. The difficulty seems to be in the fact that the precipitate settles very compactly in the crucible, thus preventing the carbon disulphide from obtaining more than a surface contact with it. In some instances, the crucibles were placed in beakers, covered with carbon

disulphide, and allowed to stand for twenty-four hours, without any appreciable difference becoming manifest in the result.

Metallic Arsenic. As.

In the oxidation of the metallic arsenic, a difficulty was encountered, which the previously mentioned minerals had been free from. It was noticed that if the conditions, which were utilised with the other minerals, were followed, (viz. that the caustic potash be brought to a state of fusion and the powdered mineral then added), a volatilisation of some of the arsenic invariably occurred. In fact, so rapidly

did this take place, that barely did the mineral come in contact with the fused potash, but what the garlicky odor of burning arsenic was perceptible. To obviate this loss, the following method was found to be the best, and in fact the only one that would give accurate results. The caustic potash was introduced into the crucible carefully heated to drive out all moisture, and eventually, brought to complete fusion. The flame was now removed, and the mass allowed to cool until it was almost solid, when the powdered arsenic was carefully spread over the surface of the chilled potash. The platinum wire is now placed in position, and

+ the current closed. Should the potash have cooled to such an extent that the current will no longer pass through the mass, or at least only with difficulty, a very small flame, carefully played under the crucible, will remedy the trouble. The arsenic, if these directions are complied with, becomes gradually oxidized, and no volatilisation is perceptible. After the first ten minutes, the crucible may be gradually heated until its contents are again in a condition of fusion, and should be kept in such a state until the end of the oxidation. The current used for the operation registered one ampere in the Noblaussch ampere-metre when the potash

was completely fused. At the beginning of the oxidation, the resistance offered by the almost solid caustic potash is so great, that the current barely registers, but this is exactly the condition that is desirable for thorough results.

The current was allowed to run for thirty minutes, being reversed for the last five minutes.

The results are as follows:—

- (1) 0.0974 gram of arsenic gave
0.1813 gram of magnesium pyro-
arsenate = 90.11% arsenic.
- (2) 0.1052 gram of arsenic gave
0.1961 gram of magnesium pyro-
arsenate = 90.23% arsenic.

The very slight residues which remained after the fusions were treated with water, showed no

signs of arsenic. The filtrates from the precipitations with magnesia solution were acidulated with hydrochloric acid and hydrogen sulphide added to see if possibly some of the arsenic might be present as arsenous acid. No trace of the latter however, was found.

Another sample of the powdered metal was dissolved in nitric acid, and the arsenic determined in the manner already indicated for the previously mentioned minerals, as magnesium pyroarsenate. The filtrations and weighing were made in a porcelain Gooch crucible. The sample yielded 90.14 % arsenic.

In the two determinations of arsenic in the metallic arsenic, given above

the magnesium pyroarsenate was also weighed in porcelain Gooch crucibles.

Kammlerbergite, $(\text{M Co Fe})\text{As}_2$.

With this mineral more difficulty was encountered than with any other, and the results that are given below, were obtained only after seventeen attempts at decomposition proved unsuccessful. The method used at first, was the one which showed itself to be efficient for the decomposition of metallic arsenic, viz. 25-30 grams of caustic potash, and a current of one ampere running for thirty minutes, with five minutes reversal at the end of the oxidation. This proved an utter failure, as the residues from the fusion, showed in all cases the presence of

arsenic, while the results obtained varied from 53% - 67% of arsenic.

A former experience having shown that the incomplete oxidation might probably be due to the enclosure of particles of mineral on the platinum wire, a more frequent reversal of the current was tried. Using the same amount of caustic potash, and increasing the current strength from one to one and a half amperes, the current was reversed after the first ten minutes, and allowed to run in the opposite direction for three minutes. It was then passed up through the crucible again for five minutes, then again down through the wire for three minutes, the process being continued for thirty minutes. The results were

altogether unsatisfactory, large quantities of arsenic being found in the residues.

The amount of caustic potash was now increased from 25-30 grams to 40 grams, the nickel crucible used being $1\frac{7}{8}$ inches high and 2 inches wide. In six decompositions made under these conditions, the current in the first two had a strength of one ampere, in the second two, of an ampere and a half, and in the last two, it was increased to one and three-quarters amperes, the current being reversed in a manner similar to the one previously tried. The results in all cases were of a negative order, as arsenic was found in all of the residues.

An increase of the time limit was now tried, with satisfactory results, using 40 grams of caustic potash,

the current was allowed to act for forty-five minutes, After various attempts to ascertain the best current strength for the purpose, it was found that a current registering an ampere was the most satisfactory, nor should it be allowed to rise above this point, otherwise the decompositions are apt to be incomplete. In the oxidations given below, the current was reversed at the end of every ten minutes, for three minutes. Another phase of the operation that seems to be essential, is to have the mineral in as fine a condition as possible. Using the conditions just given, the residues from the fusions showed no arsenic, though they were most carefully examined by the wet method and also before the blowpipe. The

arsenic was precipitated as magnesium ammonium arsenate, and weighed as magnesium pyroarsenate in a platinum crucible, the filter being ignited separately, after moistening with ammonium nitrate. The results found were as follows:-

- (1) 0.1829 gram of Rammsbergite gave 0.2598 gram of magnesium pyroarsenate = 68.76% arsenic.
- (2) 0.2168 gram of Rammsbergite gave 0.3118 gram of magnesium pyroarsenate = 69.62% arsenic.

Another sample of the mineral dissolved in nitric acid, and determined as pyroarsenate gave 70.34% arsenic.

Chloanthite. $(\text{Mn. Co. Fe})\text{As}_2$

The mineral used for decomposition was a portion of the

sample from Franklin N. J. which was reported along with other minerals by Dr. Koenig, in the proceedings of the Academy of Natural Sciences of Phila. 1889. p. 184. The decompositions were made contemporaneously with those of Rammelsbergite, and for this reason, many of the unsuccessful steps made with the latter mineral were also made with the Chloanthite. The first oxidations were made with a current of one ampere, using 25-30 grams of caustic potash, and allowing the current to run for thirty minutes. As with the Rammelsbergite, so here too, only diverse results were obtained. Reversing the current every five minutes after the first ten minutes brought about a similar

condition of affairs, the results being from five to six per cent low. The addition of copper oxide as recommended by J Smith in the oxidation of pyrite (Berichte der Deutschen Chemischen Gesellschaft, vol XXIII, p. 2281) was now tried, the quantity of caustic potash used being increased at the same time. With one sample of the chloanthite, an equal amount of copper oxide was mixed, and with another sample, double the quantity of copper oxide. The other conditions were a current of one and a half amperes, a time limit of thirty minutes, with reversals of the current after the first fifteen minutes, and 40 grams of caustic potash. This combination of conditions gave no

better results than the previous one. Satisfactory results were eventually obtained under the following conditions, the copper oxide being dispensed with entirely. The current was not allowed to register above one ampere, and the best results will be obtained if it is kept slightly below this mark. Thirty minutes was found to answer for complete decomposition, but for the sake of certainty, it is advisable to allow the current to run for forty five minutes, reversing it during the last five minutes. The amount of caustic potash used was 40 grams. The results obtained were as follows:—

- (1) 0.2332 gram of chloanthite were decomposed as above. The fusion was treated with hot water, and filtered.

The filtrate was acidulated with hydrochloric acid, and warmed to expel the carbon dioxide present. On cooling the arsenic was reduced with sulphurous acid, and after the expulsion of the excess of sulphurous acid, was precipitated by hydrogen sulphide in the cold. The precipitate of arsenious sulphide was filtered on a Gooch crucible, after the solution had stood until it barely had the odor of hydrogen sulphide, and washed with cold water. The crucible and its contents were then placed in a beaker, carbon disulphide added, and allowed to stand for twenty four hours. The crucible was then removed from the beaker, its contents washed with alcohol, then with cold water, and finally dried.

for six hours at 105°C . 0,2710 gram of arsenious sulphide was found = 70.84% arsenic.

0,2899 gram of chloanthite treated in the same manner, as the preceding, gave 0,3325 gram of arsenious sulphide = 69.93% arsenic.

In the sample of the mineral analysed by Dr Koenig and reported by him, he found 70.66% arsenic.

It will be seen from the above, accurate results were obtained by weighing the arsenic as arsenious sulphide. They are however, but two, out of a large number of determinations that were made in porcelain Gooch crucibles, and the only two which gave results sufficiently close to be utilised. The amount of sulphur precipitated

with the arsenious sulphide, must have been very small, otherwise, the results, owing to the inefficiency of the carbon disulphide, would assuredly have been high. For this reason the author can not recommend the method for general use.

The residues from the fusions were carefully examined for arsenic, but none was found to be present.

Smaltite, (Co. Ni. Fe) As₂.

From the experience gained with Rammelsbergite and Chloanthite, it was found very easy to oxidize the Smaltite. The mineral used for the purpose was mixed with gangue, and therefore was first broken up, and the Smaltite picked out as carefully as possible by hand. The resultant

material, as shown by the analyses, still contained impurities. The conditions for oxidation are as follows:-

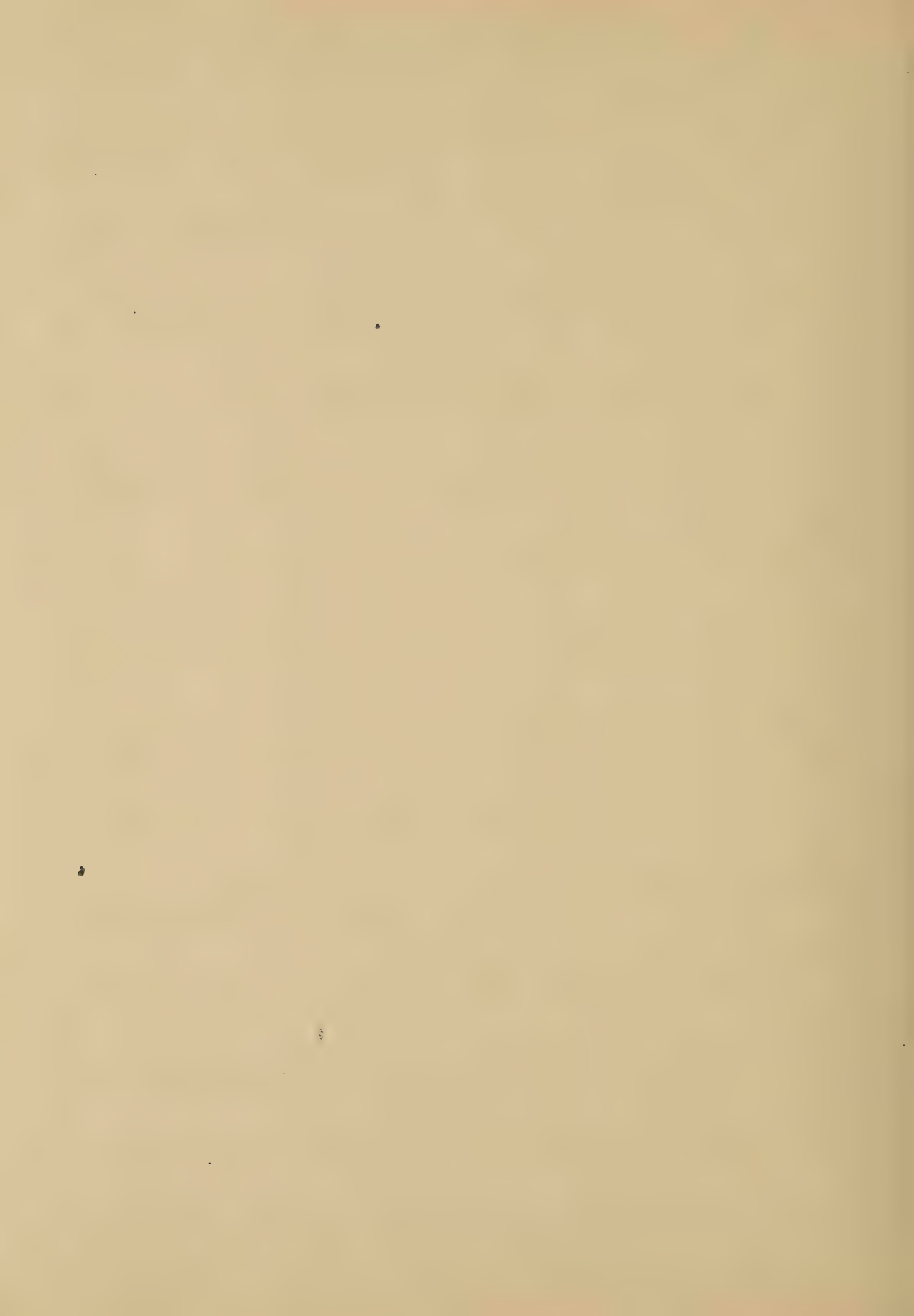
A current of one ampere with the restrictions imposed under allothite; a time limit of forty five minutes, and 40 grams of caustic potash. Using these conditions, the oxidation is complete, the residues showing not the least trace of arsenic. The results obtained were as follows:-

- (1) 0.2233 gram of smaltite gave 0.2813 gram of magnesium pyroarsenate = 60.98% arsenic.
- (2) 0.1790 gram of smaltite gave 0.2199 gram of magnesium pyroarsenate = 59.47%

The method of procedure resembled one already given. The fusion was acidified with hydrochloric acid,

then made alkaline with ammonium hydroxide, and the arsenic precipitated with magnesia solution, being finally weighed in a platinum crucible. In the latter of the two determinations, the garlic odor of arsenic was noticeable on igniting the filter paper, although it had previously been thoroughly saturated with a concentrated ammonium nitrate solution. This accounts for the slightly low result obtained, but it was not thought necessary to repeat the operation, since the residue showed that the oxidation was complete.

0,3136 gram of the ore, dissolved in nitric acid, and the arsenic determined as magnesium pyroarsenate in a platinum crucible gave 0,3929 gram of magnesium



Pyroarsenate = 60.65% arsenic.

A study of the composition of Cammelsbergite, Chloanthite and Smeltite will show several points of interest. It will be seen from their formulas, that they each contain two atoms of arsenic to the molecule, while niccolite, cobaltite, arsenopyrite etc, either have one atom of arsenic to the molecule, or have one atom of arsenic replaced by sulphur. Returning to the study of the conditions necessary for oxidation, it will be remembered that the amounts of caustic potash necessary, and the extents of time were larger for the first three minerals, than for any of the others, while the oxidations themselves seem to proceed with greater difficulty. A cause for

this, that might be advanced, is that the oxides of the metals, are united with greater tenacity to the two arsenic atoms, than they are to one, and hence require a greater expenditure of force for their separation. A somewhat similar occurrence was noticed by Dr. Smith in the oxidation of the metallic sulphides, Pyrrhotite, whose formula is in all probability, either $\text{Fe}_{11}\text{S}_{12}$ or FeS , is decomposed with great readiness, while Pyrite which contains two atoms of sulphur to the molecule, succumbed only after repeated and many fruitless trials. What might be considered a curious feature in the oxidation of these arsenides, is the fact that those containing two atoms of arsenic to the molecule, are decomposed more readily by weak currents than they are by strong ones, while with

the arsenides containing but one atom to the molecule, either strong or weak currents are equally efficacious. The only explanation that there is to offer for this seeming anomaly, is the one already given, viz: the enclosure of particles of metal on the platinum wire. In those arsenides containing but one atom of arsenic to the molecule, the decomposition is in all probability so rapid, that any enclosure of the mineral on the wire is practically impossible. In minerals like Rammelsbergite and Chloanthite, we may assume that the decomposition proceeds by much slower stages, so that if the current is sufficiently strong to deposit metal on the Kathode, there is constantly present sufficient undecomposed mineral to be enclosed in the deposited metal.

Cobaltite, (Co, Fe) As S.

This mineral was decomposed with great ease, a result to be expected, if we trace the similarity in composition between it and such minerals as gersdorffite, niccolite, etc. The conditions for oxidation are very similar to those of Gersdorffite, with the difference, that while in the latter the current was allowed to run only for twenty minutes, in the decomposition of cobaltite, it ran for thirty minutes, with a five minutes reversal at the end. Otherwise the conditions for oxidation, and for the subsequent decomposition of the fusion and for the estimation of the arsenic, are the same as for Gersdorffite. The magnesium pyroarsenate was weighed in platinum Gooch crucibles, the method being very accurate, owing to the fact that there is no possibility of any volatilisation

of the arsenic, and more rapid than weighing in a porcelain Gooch crucible, since the platinum crucible attains a constant temperature in a very short period of time.

The results obtained were as follows:-

- (1) 0,1032 gram of cobaltite gave
0,1006 gram of magnesium pyro-
arsenate = 47.2% arsenic.
- (2) 0,1326 gram of cobaltite gave
0,1313 gram of magnesium pyro-
arsenate = 47.93% arsenic.
- (3) 0,2250 gram of the same ore was
dissolved in nitric acid, the acid evap-
orated, the solution made alkaline with
ammonium hydrate, and the arsenic pre-
cipitated with magnesia solution. The
magnesium ammonium arsenate was
ignited in a porcelain Gooch crucible
and gave 0,2229 gram of magnesium
pyroarsenate = 47.96% arsenic.

Orpiment. As_2S_3 .

The preliminary investigations made with this mineral, showed that it came under the same category as the metallic arsenic. When the finely-powdered mineral was introduced into the molten caustic potash, a volatilisation of the arsenic, recognisable by its odor, occurred. The precautions given under metallic arsenic, regarding the cooling of the caustic potash and the regulation of the current, were then introduced, with successful results. Some difficulty may at first be experienced in obtaining correct control of the operation, but a few oxidations will give the operator sufficient experience to bring the decomposition to a successful completion. The conditions best adapted for the work are a current of one ampere, 25-30 grams of caustic potash, the current being allowed

to run for thirty minutes. Using these conditions, no arsenic was found in the slight residues which remained after decomposing the fusion, nor was any odor of arsenic perceptible during the entire course of the operation.

- (1) 0.1443 gram of orpiment gave 0.1761 gram of magnesium pyroarsenate = 59.08% arsenic.
- (2) 0.1044 gram of orpiment gave 0.12805 gram of magnesium pyroarsenate = 59.38% arsenic.
- (3) 0.2233 gram of the same ore dissolved in nitric acid and the arsenic weighed as magnesium pyroarsenate in a platinum crucible gave 0.2755 gram of magnesium pyroarsenate = 59.72% arsenic.

Proustite, Ag^3AsS^3

But a very small quantity of the mineral was available for analysis, and even that was intimately mixed with argenticite, no attempt was made to extract the former mineral by hand picking, instead, the entire

mixture was placed in an agate mortar and ground, the grindings then being passed through a sieve. This removed all the proustite, with some of the argentite, the greater portion of the latter remaining behind as flattened plates. Sufficient argentite however remained with the proustite, to reduce in a considerable measure the percentage of the arsenic, and the deviation of the results from the theoretical, is attributable to this cause. Sufficient material was not at hand to make a check analysis, by dissolving the mineral in nitric acid and determining the arsenic in the usual manner, but as the residues were most carefully examined for arsenic, and ^{as} none was found to be present, the natural conclusion arrived at, was, that the decomposition was complete, no loss of arsenic was noticeable

during the entire operation, and the closeness of the results indicates that the decomposition of this mineral by the electric current, can be accomplished as successfully as any one of those previously described. The conditions for oxidation are as follows:—

A current of one ampere running for thirty minutes, the current being reversed during the last five minutes.

The amount of caustic potash used was 25-30 grams. Below will be found the results obtained:—

(1) 0.1589 gram of Proustite, the arsenic being weighed as magnesium pyroarsenate in a porcelain Gooch crucible gave 0.0147 gram of magnesium pyroarsenate = 4.48% arsenic.

0.2255 gram of Proustite, the arsenic being weighed as above, gave

0.0249 gram of magnesium pyroarsenate
 = 5.34% arsenic.

Besides these minerals already recorded, several others were subjected to oxidation by the current, but owing to lack of material for the continuation of the work, satisfactory conclusions were not reached. The results are however, of interest, and are therefore here appended.

Domaykita or niccolite, $n(\text{NiAs}) + m(\text{Cu}^3\text{As})$.

The mineral used for oxidation came from Makipicoten island, and was a small section of a specimen in the mineral collection of the University of Penna, incorrectly labeled Whitneyite. Two oxidations of the mineral, in which the residues still showed arsenic, gave to the surprise of the author, 35.3% 40.04% of arsenic respectively, showing that the mineral could not be Whitneyite,

Since this should contain theoretically 11.64% of arsenic. A later oxidation gave using 0.2207 gram of the mineral, 0.2016 gram of magnesium pyroarsenate = 44.22% of arsenic. 25-30 grams of caustic potash were employed, with a current of 1-1½ amperes for thirty minutes, reversing the current at the end for five minutes. In this oxidation no trace of arsenic was found in the residue. On reporting the results obtained to Dr. Koenig, he made an analysis of another sample, by dissolving the mineral in nitric acid, and found it to contain 47 % of arsenic. This result is however, not inharmonious with the last one obtained by oxidation with the current, since in a fresh fracture of the mineral, the niccolite and domoykite can be seen lying along side of each other. Owing to this

non-homogeneity, the sample analysed by Dr Koenig may have contained more niccolite than the sample oxidized by the current, and gave proportionately a higher percentage of arsenic. Unfortunately the scarcity of the mineral necessitated the discontinuance of the work, and the question of complete oxidation is still in doubt. The few percent difference in the results obtained by the two methods, however, indicates, that the decomposition can be successfully accomplished, under the conditions mentioned above,

Enargite - $3\text{Cu}^2\text{S} \cdot \text{As}_2\text{S}_5$.

The material used for decomposition, contained an admixture of gangue, and as with the domingite, not sufficient of the substance was obtainable, to settle thoroughly the question of oxidation. As the percentage of arsenic found, is

within the neighborhood of what the mineral ought to contain, and as no arsenic was detectable in the residue from the fusion, the result obtained is here appended, without any definite statement regarding the thoroughness of the method. The amount of caustic potash used in the oxidation was 25-30 grams, the current strength, one ampere, with a reversal of the current at the end of the operation, for five minutes. The arsenic was determined by weighing in a porcelain Gooch crucible as magnesium pyroarsenate.

0.2840 gram of Enargite gave 0.0770 gram of magnesium pyroarsenate = 13.12% arsenic.

The theoretical percentage of arsenic in the mineral is 19.1%. If we remember, however, that the sample used contained gangue, and that no arsenic was found in the residue, it is but fair to assume that the result lies within the limit of error, and that the oxidation is complete. No positive statement, however, can be made.

A study of the methods used for the determination of the arsenic in the various oxidations will be of interest. As has already been stated, the determination of the arsenic as arsenious sulphide by weighing in a porcelain Gooch crucible, can not be recommended, owing to the great difficulty experienced in removing the sulphur with which the precipitate of arsenious sulphide is contaminated. The more common method of weighing the arsenic was found to be accurate, if the conditions laid down for this determination are complied with, the method requiring at the same time, great care. In the incineration of the filter, from the magnesium ammonium arsenate constant vigilance was required to prevent a volatilization of a portion of the arsenic, even though the filter had

been previously saturated with a concentrated ammonium nitrate solution, and in many cases, it was necessary to moisten the burnt filter several times with the solution, before it could be completely reduced to ash. Weighing the precipitate in either a porcelain or platinum Gooch crucible removes this source of error, and is of all the methods so far mentioned the most to be recommended. In the precipitations with magnesia solution, it was noticed that the presence of large quantities of alkaline salts, have a tendency to materially retard the precipitation of the magnesium ammonium arsenate, and it frequently became necessary to allow the solution to stand at least forty-eight hours before the precipitation was complete. For this

reason when large quantities of alkaline salts are known to be present, for example, the caustic potash used in the fusion, it may be more advisable to reduce the arsenic with sulphurous acid, precipitate it as arsenious sulphide, filter and wash, and then to convert it into arsenic acid by dissolving in nitric acid, and determine as magnesium pyroarsenate.

Owing to the time and care required in the above determinations, the method described in Sutton's volumetric analysis, 6th edition, as recommended by Pearce, of the Colorado Smelting Company, was tried. The substance of the method is as follows:—

"The arsenic brought into the form of"
 "alkaline arsenate, is acidified with nitric"
 "acid, and boiled to remove carbon dioxide"

"and nitrous fumes. It is then cooled to the
"ordinary temperature, and almost exactly
"neutralised as follows:- Place a small
"piece of litmus paper in the liquid: it
"should show an acid reaction, now grad-
"ually add strong ammonia until the litmus
"turns blue, avoiding a great excess, Again
"make slightly acid with a drop or two
"of strong nitric, and by means of very
"dilute ammonia and nitric acid, added
"drop by drop, bring the solution to such
"a condition, that the litmus paper, after
"having previously been reddened, will
"in the course of half a minute begin
"to show signs of alkalinity. The litmus
"paper may now be removed and
"washed, and the solution if tolerably
"clear, is ready for the addition of
"silver nitrate. If the neutralisation
"has caused much of a precipitate

(alumina etc), it is best to filter it off "at once, to tender the subsequent filtration and washing of the silver arsenate easier" - The latter portion of the process consists in determining the silver in the silver arsenate, and calculation the percentage of arsenic from the amount of silver found.

A number of determinations were made by the author to ascertain the value of the method, but all of the attempts made, resulted in failure. It was found well nigh impossible to tell by the color of the litmus paper, whether the solution was acid or alkaline. In several cases, "methyl orange" was used as an indicator, and while the solution was made slightly alkaline as recommended by Pearce, the addition of ammonia to the filtrate, invariably brought down considerable

quantities of silver arsenate, and the results obtained were proverbially low. The silver was not determined by titration as recommended by Pearce, but by electrolysis. The best result obtained by this method, with the details of the operation are given below:-

A sample of Ramsdellbergite was decomposed under the conditions given for that mineral. The fusion was decomposed with hot water, the insoluble material filtered off, and the clear filtrate acidified with nitric acid, and boiled to remove the carbon dioxide. On cooling, ammonium hydroxide was added, the precipitated alumina etc. filtered off, and the additions of dilute nitric acid, and dilute ammonia made according to Pearce's directions, until the solution became faintly yellow, methyl orange

Having been used as an indicator, Silver nitrate was now added, the solution stirred and the precipitate of silver arsenate filtered off. The addition of a drop of ammonia to the clear filtrate gave a further precipitation, and ammonia was added until the precipitation was supposed to be complete. The two precipitates were then united, washed with cold water, dissolved in nitric acid, and the excess of acid evaporated. To the solution, ammonium hydrate was added until the solution became alkaline, and then an excess of potassium cyanide, ~~and~~ the solution decolorised, and the resultant silver weighed, 64.21% arsenic were found, the same sample giving by the pyroarsenate method 70.34% arsenic.

The author believes that with continued

Practice, sufficient dexterity might be obtained with this method to obtain accurate results, but it is hardly one that could be recommended for work outside of a technical laboratory, where absolute accuracy is not so important a feature as that the results should be correct relatively to each other.

A comparison of the oxidation of the metallic sulphides with that of the metallic arsenides, shows several points of difference. In the oxidation of the sulphides, it was observed by Dr Smith, that the process was completed in three stages, the sulphur being first oxidized to hydrogen sulphide, then to sulphurous acid, and eventually to sulphuric acid. A similar state of affairs was not observed with the arsenides, and

the oxidation evidently proceeds directly from metallic arsenic to arsenic acid.

Even in samples where the oxidation had not been complete, and where the residues still showed undecomposed mineral, the filtrates from the fusion showed no trace of arsenious acid, after the alkaline arsenate had been removed by precipitation with magnesia solution.

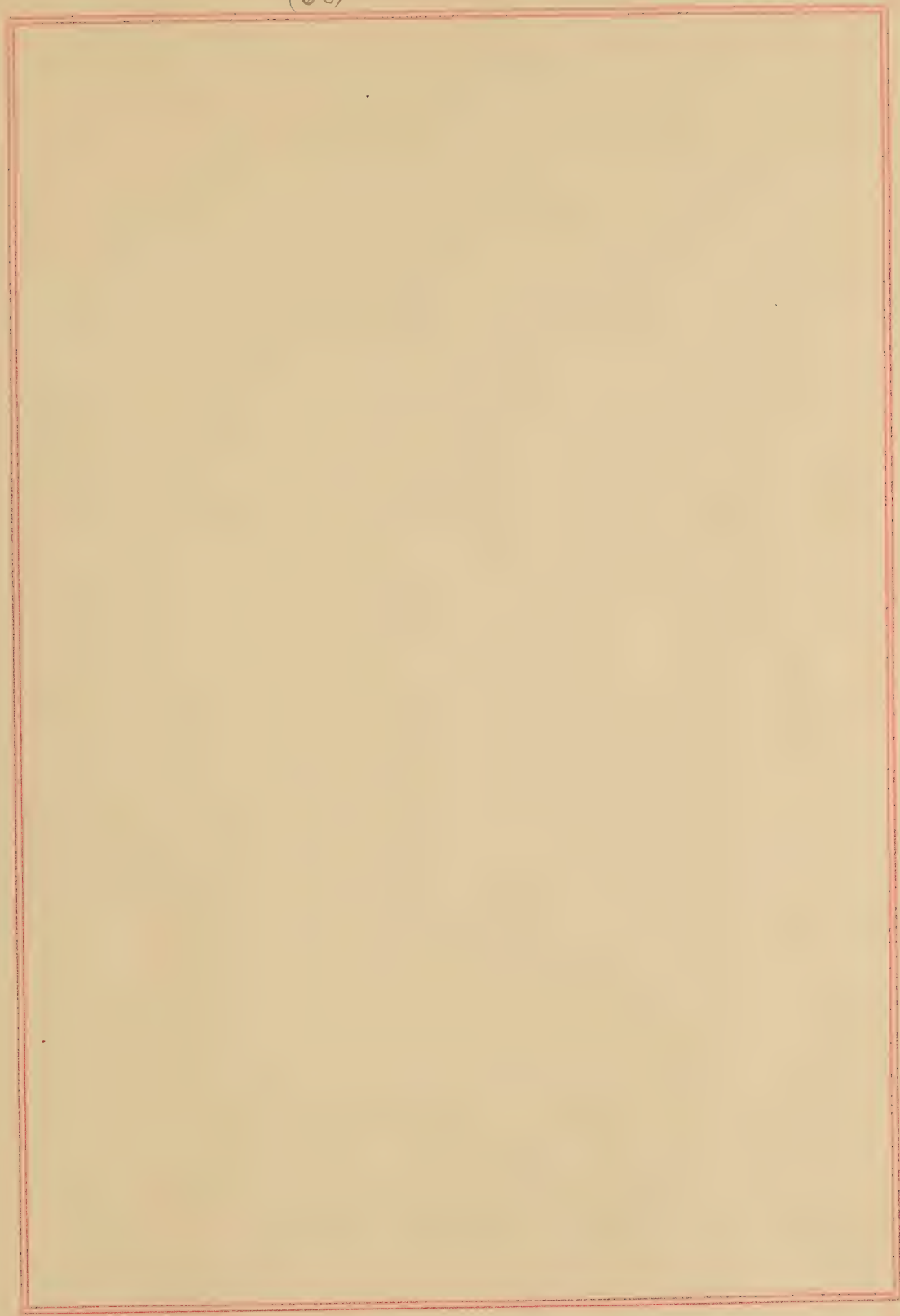
Regarding the time limit, the amount of caustic potash needed, strength of current etc required for the oxidation of these two classes of compounds, no marked differences are noticeable, and, as been already shown, the degrees of difficulty encountered in decomposing them, seem to vary in a ratio, dependent chiefly on the chemical composition of the mineral.

In conclusion, the author would here express his sense of deep obligation to Prof. Edgar F. Smith for his unremitting kindness during the progress of the above work, and for his constant help in assisting its completion.

Thanks are also due to Prof. George A. Koenig, for samples of minerals, and to Mr. D. L. Wallace, of this laboratory, for assistance rendered in the oxidations.

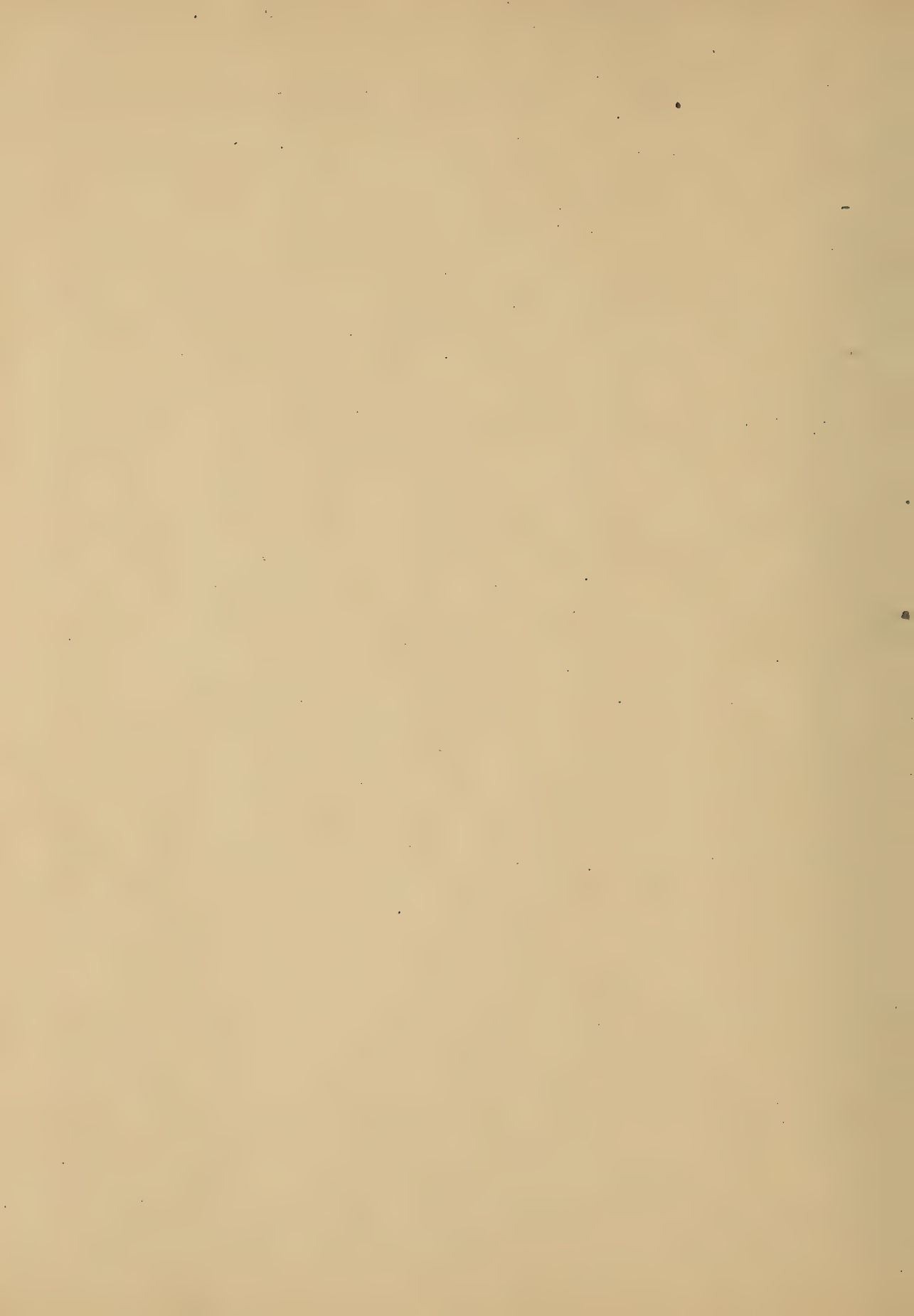
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POP 1892

Frankel

The oxidation of metallic
arsenides by the electric current

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